CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

It is interesting to observe that the primary aim of the theoretical chemistry has been to design models useful for understanding the structures of different molecular systems. The class of compounds termed complexes or the coordination compounds invited the attention of the scientists since 1798 when Tassert observed the formation of an orange product on combination of ammonia and cobalt (III) salt. The preparation of several such compounds followed and it was noted that the normal properties of the metal ions are suppressed in such compounds. In a general way such complex compounds can be defined as "species formed by the association of two or more simpler species, each capable of independent existence".

Werner first proposed that in the complex compound $CoCl_3.6(NH_3)$, the ammonia molecules are linked to the central cobalt ion by nonionisable auxiliary valency, the primary valency of the metal ion being satisfied by the ionisable chloride ions. With the advent of electronic theory of valency, Sidgwick interpreted the auxiliary valency as a special case of covalent bond, formed by the donation of a pair of electrons from the ligand to the metal ion. The metal ion thus attains the effective atomic number same as the atomic number of the nearest inert gas and this accounts for the stability of the complex.

However, ever since the first application of quantum mechanics to hydrogen molecule in 1927, it became clear that ultimate description of the molecular systems had to be based on the new quantum concepts. The two quantum mechanical approximations put forth to explain the structure of covalent molecules are valence bond theory and molecular orbital theory. Pauling first applied valence bond theory to complex formation[1]. According to this the interaction of vacant metal ion orbitals and filled ligand orbitals results in the formation of complexes with various shapes and magnetic properties. The vacant d, s and p orbitals of the metal ion being closer in energy, undergo hybridization and this results in the formation of octahedral, square planar or tetrahedral structures. According to group theory, for the structures with D_4h, Td and Oh symmetry, the metal orbitals involved in hybridization are S; Px; Py; Pz, $d_{x^2-y^2}$, S, Px, Py and $d_{x^2-y^2}$; d_{z^2}, Px; Py; Pz, respectively. If vacant d orbitals are not available in the metal ion, pairing of the electrons takes place in d_{xy}, d_{xz} and d_{yz} orbitals thus vacating $d_{x^2-y^2}$ and d_{z^2} orbitals. The redistribution of electrons during complex formation is visualised from the associated changes in the magnetic properties. Pauling's concept was extended to incorporate the hybridizations of the type sp^3d^2 and p^3d which result in what are known as outer orbital complexes.

In all the above cases the resulting bonds are σ in character. Pauling also considered the possibility of interaction between d_{xy}, d_{xz} and d_{yz} orbitals of the metal ions with π symmetry with vacant $d\pi$ or $p\pi$ orbitals of the ligand atom. The σ and π bonds are considered to mutually stabilize each other thus resulting in more stable M-L bond. The stabilities of the cyanide complexes and carbonyl complexes have been attributed to $d\pi$-$p\pi$ interaction and the stabilities of M-P, M-As and M-S bonds have been explained in terms of $d\pi$-$d\pi$ interaction. However, Pauling's theory is qualitative in nature and does not provide explanation for spectral characteristics of the complexes, their detailed magnetic properties and the relative stabilities of the complexes with different structures.

The molecular orbital theory was, therefore, introduced in 1935 by Van Vleck[2,3] to explain the formation of complexes. According to him linear combination of metal and ligand atom orbitals results in the formation of bonding and antibonding molecular orbitals. In the complexes with Oh point symmetry, the ligand atom orbitals combine to form composite orbitals of a_1g, t_1u and eg symmetry. $d_{x^2-y^2}$(eg), 4s(a_1g) and 4p(t_1u) orbitals of the metal ions combine with the ligand composite orbitals of same symmetry resulting in the formation of six bonding and six antibonding molecular orbitals. The electrons are filled up in the molecular orbitals in the increasing order of energy. The orbitals formed are all σ in character. In cases where π orbitals are available on the ligand atom, they combine to form the composite orbitals having the required symmetry to combine with metal d_{xy}, d_{xz} and d_{yz} (t_2g) orbitals and this results in the formation of the bonding and antibonding π molecular orbitals. The redistribution of electrons in the molecular orbitals liberates energy and thus stabilizes the complexes.

The above theories, however, give too much stress to the covalent character of M-L bond. Van Arkel and De Boer were first to consider the M-L bonding to be entirely electrostatic in nature and this was supposed to arise due to an attraction between the positively charged metal ion and the ligand anion or negative end of the ligand dipoles. Though this theory can explain the formation of different structures and their stabilities, but it has some limitations. It fails to explain the spectra and magnetic properties of the complexes. Bethe and Van Vleck[4,5] adopted an extended electrostatic concept known as crystal field theory. They pointed out that the charges on the ligand create an electrostatic field of very high intensity around the metal ion and this creates perturbation in the metallic d orbitals. Out of the five d orbitals, the lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals are directed along the axës and hence in an octahedral complex they are directly exposed to the ligand field. The electrons having maximum probability of occuring along these paths are subjected to greater forces of repulsion from the ligands than those in the d_{xy}, d_{xz} and d_{yz} orbitals. Hence, under the influence of an approaching ligand, the five d orbitals, originally degenerate, split into two separate sublevels of differing energy. The orbitals lying in the direction of the ligand are raised in energy in comparison with those which lie in between the ligands. Application of group theory shows that the high and low energy sets have, respectively, eg and t_2g symmetry. Thus the crystal field theory can be said to be an intra-complex stark effect in which the external electrostatic field operating on the central metal ion arises from the charge distribution in the ligand system.

The amount of energy by which the higher doubly degenerate eg orbitals are separated from the lower triply degenerate t_2g orbitals is termed crystal field splitting (Δ or 10Dq) and the value is dependent on the intensity of the electrical field created by the ligands. The extent of crystal field splitting is dependent on two factors. If the charge upon the central metallic ion is high, the ligands are pulled closer to the central metallic ion and creates a higher amount of splitting. Secondly, higher is the charge on the ligands directed to the metal ion, higher is the repulsive effect exerted and greater is the splitting.

It is a quantum mechanical requirment that the average energy of the perturbed d-levels should remain unchanged. According to this, if we add up the crystal field energy of the four eg electrons and six t_2g electrons we should get zero. Consequently, the eg orbitals are raised by 6Dq, while t_2g orbitals are lowered down by 4Dq. The rearrangement of electrons in the lower lying orbitals, results in gain in energy called Crystal Field Stabilization Energy (CFSE). When the crystal field splitting is more than pairing energy, the electrons get paired in lower d orbitals. However, in cases of weak fields, the splitting brought by the crystal field is small and electrons tend to remain unpaired giving rise to high spin complexes with lower crystal field stabilization energy. Thus the crystal field theory explains the formation of Pauling's low and high spin complexes.

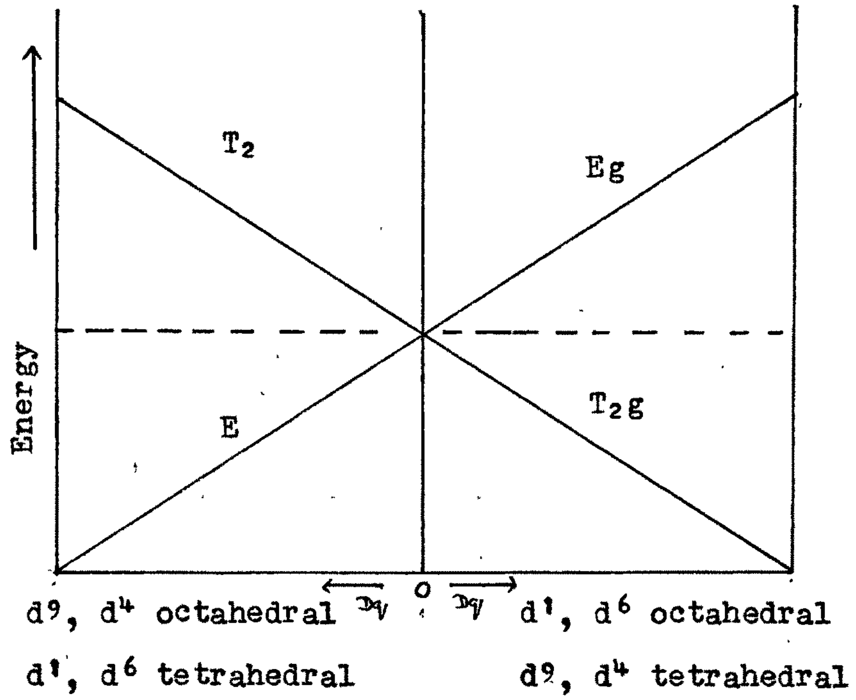
In the field with D_4h or Td symmetry, the metal d orbitals get resolved in different ways. In the former the t_2g orbitals further get split up into a nondegenerate and a doubly degenerate state and the eg state splits up in two nondegenerate states. In tetrahedral complexes the high energy orbitals have t_2g symmetry and low energy orbitals have eg symmetry. Since in the tetrahedral field ligands are not exactly directed towards the t_2g orbitals, for the same ligand, crystal field splitting Δ has smaller value in a tetrahedral complex than in octahedral complex. The tetrahedral complexes are, therefore, less frequent.

Absorption spectra of metal complexes :

Crystal field theory extends a satisfactory explanation for the spectra of complexes. For d^1 case ground state is ^2D. Due to octahedral crystal field it gets split into T_2g (lower) and Eg (higher) states. The transition of electron from T_2g to Eg absorbs energy in the visible range and a peak is observed in the absorption spectrum as in the case of $[Ti(H_2O)_6]^{3+}$ [6].

When we deal with ionic systems having more than one but less than nine "d" electrons, the number of terms which arise in the free ions are, for d^2 or d^8, 3F, ^1D, 3P, ^1S and ^1G, for d^3 or d^7, ^4F, 2G, ^4P, 2P, 2H, [illegible]..., for d^4 and d^6, ^5D, ^3H, ^3G, ^3D, ^3P, and for d^5, ^6S, ^4G, ^4P, ^4D, ^4F. The Orgel diagram[7] shows how the ground spectral terms are split up by the weak crystal fields of different intensity. The diagram is simplest for the splitting of a D term. This is shown in figures (1) and (2) for the ground state term in d^1, d^4, d^6 and d^9 systems.

Figure 1



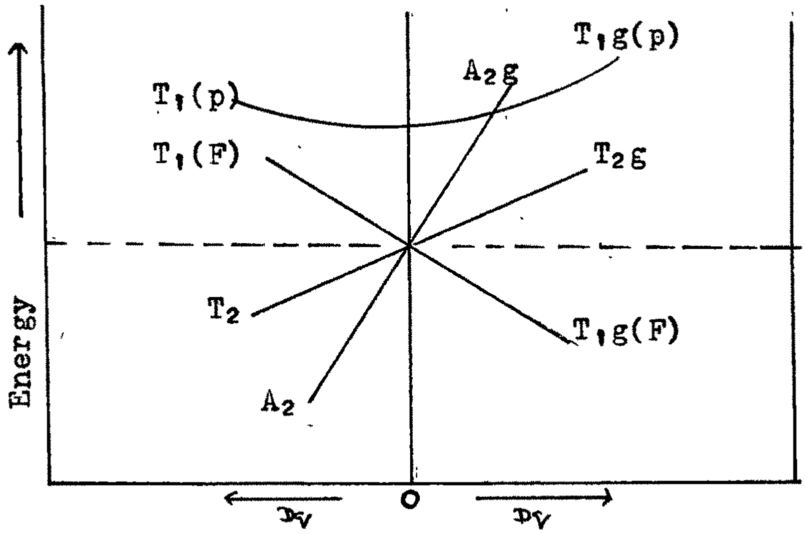
(Orgel diagram for d^1, d^4, d^6 and d^9 complexes).

In d^2, d^3, d^7 and d^8 systems the splitting of F and P terms, with maximum spin have been shown in figure (2).

The Orgel diagram for octahedral vanadium(III) as seen in figure (2) predicts three spin allowed transitions. These are

ν_1 $^3T_1g(F) \longrightarrow {}^3T_2g(F)$
ν_2 $^3T_1g(F) \longrightarrow {}^3T_1g(P)$
ν_3 $^3T_1g(F) \longrightarrow {}^3A_2g$

Figure 2



(Orgel diagram for d^2, d^3, d^7 and d^8 complexes).

Further-more it predicts that ν_1 will be lowest in energy. Dq may be determined from the Orgel diagram. Thus, by using the absorption spectra, it is possible to calculate the Dq values in case of the complexes of same metal ion with various ligands and the ligands can be arranged in a sequence of their field strengths. Such a series is known as spectrochemical series.

In Tanabe and Sugano[8] diagrams, however, splitting of all possible states in both weak and strong field is shown.

$Cu^{2+}(d^9)$ and $Ni^{2+}(d^8)$ have, respectively, ^2Eg and ^3A_2g ground states in octahedral field and ^2T_2g and ^3T_1g ground states in the tetrahedral field. On absorption of energy the transition to higher energy states is possible. Since the absorption in the ultraviolet or visible range requires a change in dipole moment, the following selection rules govern the absorption spectra of the complexes.

(1) Transitions between the states of different multiplicity are multiplicity forbidden.

(2) In a molecule which has a centre of symmetry, $g \longrightarrow g$ and $u \longrightarrow u$ transitions are Laporte forbidden.

(3) Simultaneous excitation of more than one electron is not allowed.

Thus in accordance with the second condition, no d-d transition should be allowed in octahedral complexes. However, due to vibronic coupling, the Laporte forbidden transitions are allowed in the octahedral complexes. They result in absorptions of low intensity.

In accordance with the above rules, the following transitions should occur in Ni^{2+} octahedral complexes.

$$^3A_2g \longrightarrow {}^3T_2g(F)$$
$$^3A_2g \longrightarrow {}^3T_1g(F)$$
$$^3A_2g \longrightarrow {}^3T_1g(P)$$

These are all Laporte forbidden and hence extinction coefficients are low. The first one is a low energy transition and is observed in the near I.R. region. The second one occurs in the visible range and the third is a high energy transition appearing in the ultraviolet region. This is true for a symmetrical octahedral field. In case of octahedral Ni^{2+} complexes with nonequivalents ligands, the Oh symmetry gets reduced to D_4h (distorted octahedral or square planar). This involves further splitting of the spectral state and hence the nature of the spectrum undergoes a change.

In the tetrahedral field the transitions possible are

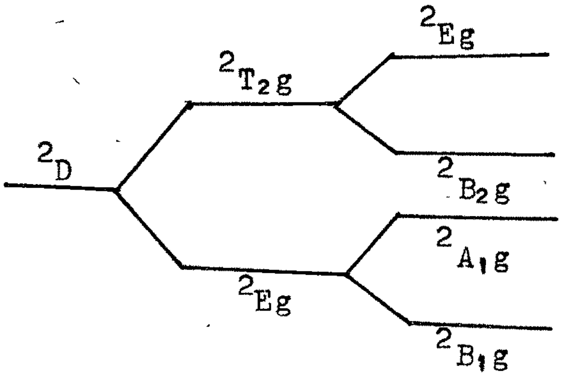
$$^3T_1g(F) \longrightarrow {}^3T_2g(F)$$
$$^3T_1g(F) \longrightarrow {}^3T_1g(P)$$
$$^3T_1g(F) \longrightarrow {}^3A_2g(F)$$

Since the tetrahedral complexes have no centre of symmetry, the d-d transitions are allowed and hence the extinction coefficients of the peaks in the spectra of tetrahedral Ni^{2+} complexes are expected to be high[9].

In case of Cu^{2+} complexes (d^9) there should be expected only one transition in both octahedral ($Eg \longrightarrow T_2g$) and tetrahedral ($T_2g \longrightarrow Eg$) complexes.

However, in accordance with Jahn-Tellor theorem[10] the octahedral Cu^{2+} complexes undergo distortion. As a result of it, there is further splitting of the t_2g and eg orbitals and the redistribution of electrons results in the liberation of extra amount of energy and this stabilises the complex. Consequently both the spectral states ^2Eg and ^2T_2g undergo further splitting into two components each as shown in the following figure (3) :

Figure 3



Three transitions should, therefore, be possible corresponding to $^2B_1g \longrightarrow {}^2A_1g$, $^2B_1g \longrightarrow {}^2B_2g$ and $^2B_1g \longrightarrow {}^2Eg$. These bands are closely spaced and in some cases may overlap each other.

The crystal field theory can thus provide an explanation for the spectra produced due to d-d transition in the transition metal ions. It can also explain the magnetic, stereochemical, thermodynamic and kinetic properties of the complexes. But most serious limitations of the theory is that it does not consider any interaction between metal and ligand orbitals. It cannot, therefore, explain charge transfer bands produced due to transition of electrons from ligand to metal ion. It does not also account for π bonding which is of significant importance, in several transition metal complexes.

It also fails in the cases of complexes wherein the occurence of forbidden d-d transition bands is explained by the consideration of mixing of metal d orbitals with the ligand orbitals. Further the energy of ground 3P states of Ni^{2+} ion in complexes, obtained from absorption spectral data, is found to be less than the free Ni^{2+} ion value as obtained from emission spectral studies.[11] This decrease has been attributed to the increase in the distance between metal d electrons in the complex due to the expansion of d electron clouds of the metal ions on the ligand atom orbitals. Widening of the d electron cloud is termed Nephalauxetic effect.[12] The common ligands can be arranged according to their ability to cause cloud expansion. This series, similar to spectrochemical series is termed Nephalauxetic series. The presence of M-L covalent interaction has also been substantiated by magnetic, NMR, ESR and Mossbauer studies.[13]

An alternative theory was, therefore, suggested by the joint attempt of a number of chemists.[14] It is termed ligand field theory. It is a hybrid approach in which the computational advantages of the crystal field theory are preserved, but it considers that certain parameters should be changed in order to account for some amount of covalent interaction between metal and ligand orbitals. Unlike the crystal field theory it considers that inter-electronic parameter in complexes are not same as in the free metal ion, but it undergoes variation depending on the extent of the metal ligand orbital overlap. The Racah parameter β, which is a measure of the inter electronic repulsion in the free metal ion, undergoes a lowering in complexes. The extent of lowering is a measure of the amount of covalent interaction. Therefore, the ligand field theory has been termed as adjusted crystal field theory by Cotton[15] and can be considered as a compromise between the crystal field and molecular orbital theories.

The stability of the complex compounds :

Another aspect of the study of the complex compounds is to determine their stabilities in solution. The publication of Bjerrum's dissertation in 1941 opened the doors for the advancement of research in the field of complex compounds.

According to him the complex formation is a stepwise reaction as follows :

$$M + L \rightleftharpoons ML \qquad (1.1_1)$$

$$ML + L \rightleftharpoons ML_2 \qquad (1.1_2)$$

$$ML_{i-1} + L \rightleftharpoons ML_i \qquad (1.1_i)$$

$$ML_{N-1} + L \rightleftharpoons ML_N \qquad (1.1_N)$$

M = metal ion, L = ligand. The charges on the ligand ions have not been shown. The equilibrium constant governing each step is, termed the stepwise formation constant. For a complex of the type (ML_2)

$$K_1 = \frac{[ML_1]}{[M]\,[L]}$$

$$K_2 = \frac{[ML_2]}{[ML]\,[L]}$$

and

$$\beta_2 = K_1K_2 = \frac{[ML_2]}{[M]\,[L]^2}$$

In solution there is a competition between the hydrogen ion and the metal ion to combine with the ligand ion. If it is L^{2-}, two hydrogen ions can combine in steps :

$$L^{2-} + H^+ \rightleftharpoons LH^-$$

$$LH^- + H^+ \rightleftharpoons LH_2$$

Equilibrium constants govern each step and are known as first and second proton ligand stability constants. β_2^H can be defined as the product of K_1^H and K_2^H.

Bjerrum introduced the term degree of formation $\bar{n}$

which can be defined as the average number of ligands bound per metal ion.

$$\bar{n} = \frac{[ML_1] + 2[ML_2] + \text{------} N[ML_N]}{[M] + [ML_1] + [ML_2] \text{---} [ML_N]} \qquad (1.11)$$

It is now assumed that ionic or molecular species involving H, L and M other than those given in the above equilibria, do not exist in solution. This is equivalent to assuming the absence of polynuclear complexes and proton bearing complexes.

Substituting for the value of ML_i from equation of the type

$$K_i = \frac{[ML_i]}{[ML_{i-1}][L]}$$

applied to equilibria (1.1_1) and (1.1_2) ...... (1.1_N), and eliminating $[M]$, the resulting expression would be ,

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2 + \ldots + N.K_1K_2\ldots K_N[L]^N}{1 + K_1[L] + K_1K_2[L]^2 + K_1K_2\ldots K_N[L]^N} \quad ..(1.12)$$

which may be arranged in the form

$$\bar{n} + (\bar{n} - 1)K_1[L] + (\bar{n}-2)K_2K_1[L]^2 + \ldots(\bar{n}-N)K_NK_1K_2[L]^N = 0 \quad (1.13)$$

This equation or equation (1.12) was termed " formation function " by Bjerrum.[16]

A similar function for the proton ligand complex is given by

$$\bar{n}_H = \frac{K_1^H[H] + 2K_1^H.K_2^H[H]^2 + \ldots + jK_1^H.K_2^H\ldots K_j^H[H]^j}{1 + K_1^H[H] + K_1^H.K_2^H[H]^2 + K_1^H.K_2^H\ldots K_j^H[H]} \qquad (1.14)$$

where $\bar{n}_H$ is the mean number of proton bound per noncomplex bound ligand molecule using the equation

$$\beta_i^H = \frac{[LH_i]}{[H]^i\,[L]} = \prod_{i=1}^{i} K_i^H \quad ..$$

$\bar{n}_H$ is written as

$$\bar{n}_H = \sum_{i=0}^{j} i\beta[H]^i \Big/ \sum_{i=0}^{j} \beta_i^H [H]^i \qquad (1.15)$$

since the total amount of the same metal salt and the chelating agent introduced into the solution are known, the following reaction can be stated :

$$T_M = \sum_{i=0}^{N} [ML_i] \qquad (1.16)$$

and

$$T_L = \sum_{i=0}^{j} [LH_i] + \sum_{i=0}^{N} i[ML_i] \quad (1.17)$$

from the equation

$$\beta_i = \frac{[ML_i]}{[M][L]^i} = \prod_{i=1}^{i} K_i$$

the equation (1.16) can be written as

$$T_M = [M] \sum_{i=0}^{N} \beta_i [L]^i \qquad (1.18)$$

and using the equation for β_i as shown above and equation also for β_i^H , the expression becomes

$$T_L = [L] \sum_{i=0}^{j} \beta_i [H]^i + [M] \sum_{i=0}^{N} i\beta i[L]^i \qquad (1.19)$$

In the above equations K_i^H , K_i are called i^{th} proton ligand stability and i^{th} stoichiometric metal ligand stability constants, respectively, and T_M and T_L are the total concentrations (in gram mole per litre) of M and L present in a solution, respectively.

The plots of $\bar{n}$ against log 1/[L] or pL are called the formation curves of the systems. The solution of these formation functions leads to stepwise metal ligand formation constants.

The statistical effects prevent the successive formation constants from being equal and the ratio between the two consecutive constants can be determined statistically provided asymmetry, chemical and electrical forces are ignored. From statistical consideration it may be assumed that the tendency of the compounds MA_n to split off groups is proportional to n, the number of groups already attached and the tendency to add an additional group is proportional to (N - n), the number of unfilled positions.

It has been shown that in a system where ML_2 is the highest complex and the spreading factor K_1 / K_2 is high, the values of pL at $\bar{n} = 0.5$ and 1.5 correspond to $\log K_1$ and $\log K_2$. This involves some presumptions and is not applicable in cases where K_1 / K_2 is low. Even in the cases where spreading factor is high it is not desirable to depend on the values of pL at specific points only, because this may involve experimental error.

Different workers, have, therefore, adopted different methods suitable to their experimental conditions. These have been reviewed by Irving and Rossotti[17] and Heraon and Gilbert.[18] Of all these methods, those suggested by Bjerrum[19] have been widely used specifically for a system where N = 2.

Factors affecting stability constants :

The stability of a complex generally depends on following major factors :

(1) Temperature

(2) Nature of the solvent

(3) Other ions present

(4) Nature of metal

(5) Nature of ligand.

While carrying out the solution studies of these complexes by Irving-Rossotti titration technique[20] the first three factors are maintained constant and hence the remaining two factors are only affecting the stability of the complexes and are being discussed in detail.

<u>The nature of metal</u> :

Among the elements, which undergo complex formation and chelation, may be included most of the metals of periodic system. It is found that there is an increase in stability constant with increasing values of e^2/r where e = charge on the metal ion and r = radius. The higher is the charge density of the metal ion greater is the stability of the complex formed. Consequently, alkaline earth metal ions form less stable complexes than transition metal ions.

The separation of rare earth ions on cation exchange column by elution with ammonium citrate buffer has been described by Ketelle and Boyd[21] and offers an interesting comparison of the effect of ionic radius on the behaviour of these ions. It was found that the sequence of relative absorbability of the trivalent ions, is La > Ce > Pr > Nd Pn > Sm > Eu > Gd > Tb > Dy > Y > Ho > Er > Tm > Yb > Lu.

This is exactly the order of the decreasing ionic radius.[22]

A similar variation in the stability of rare earth chelates of EDTA has been reported by Martell and Calvin.[23] They have observed that the selective chelation in the presence of carbonic buffer at pH ~ 8.5 takes place in the order Y $>$ Sm $>$ Nd $>$ Pr $>$ La. This is also the order of increasing ionic radius, increasing basicity and increasing absorbability on ion exchange resins.

It is interesting to note that Zn chelates have rather higher stability constants than expected on the basis of ionic radius. Though the radius of Mg^{2+} is less than that of Zn^{2+}, the stability constants of the complexes of latter are higher than that of magnesium. It seems that the zinc chelates involve bonds of a different type than those of the alkaline earths. The increased stability of zinc complexes is probably due to greater contribution due to covalent interaction in the M-L bond.

Irving and Williams[24] have shown that for a number of ligands the stability sequence for the first row bivalent transition metal ions is $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$.

This sequence is called Irving-Williams order of stability and has been shown to hold for a variety of ligands containing donor nitrogen and/or oxygen[25] and sulphur atoms.[26] Similar order has been previously observed by various authors.[27] Recently Mellor and Maley[28] have suggested a longer series including other metal ions. This expanded form of Irving-Williams[29] order is as follows :

$VO^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$

Irving and Williams regarded the second overall ionisation potential and reciprocal ionic radius of the metal ion as a measure of covalent and electrostatic contribution, respectively, to the enthalpy changes, and reciprocal ionic radius as a measure of entropy change. They suggested that the variation of these two factors gives a good account for the observed sequence. However, anamolous behaviour is observed in some cases.

In weak ligand field complexes of the metal ion with d^1, d^2 and d^3 configuration , the electrons occupy t_2g levels and contribute CFSE. In case of metal ion with d^4 to d^{10} configurations electrons are forced to occupy the eg levels, thus reducing the crystal field stabilization energy. In case of metal ions with d^0, d^5 and d^{10} configurations no CFSE is liberated. The ligand field stabilization consideration can explain the lesser stability of the Mn^{2+} and Zn^{2+} complexes. In case of d^4 and d^9 configuration additional stabilization energy is available due to Jahn-Tellor effect. This is the reason why in cases, where Jahn-Tellor stabilization is low or there are five or six coordinated donor atoms present in one ligand molecule, $d^3 > d^4$ and $d^8 > d^9$. In such cases Cu^{2+} complexes formed are less stable than corresponding Ni^{2+} complexes. Similarly for Ni(II) and Zn(II) complexes the order Zn(II) > Ni(II) is expected if CFSE contribution is less, whereas Ni(II) > Zn(II) is expected in strong field complexes.

Nature of Ligand :

Many properties of the metallic chelates are dependent on the organic molecule which combines with the metal ion. Thus, the size of the ring, the number of rings formed with a given metal ion and stabilizing or interfering resonance interactions are governed by the structure of the chelating agent. Moreover the complex formation is an acid-base reaction, in which metal acts as an acid and the ligand as the base in the Lewis sense. It can be inferred, that the ligand with a higher basicity should have a greater tendency to form complexes. A linear relationship between the stability of the complex and the base dissociation constant of the ligands has been shown by a number of scientists. The other factors in the ligand which affect the stability of the number of metallic complexes are as follows :

The size of the ring :

The work of Ley[30] on the chelates of amino acids showed that chelates with 5 and 6 membered rings are most stable. Four membered chelate rings are rare. Pfeiffer[31] has observed that in general the five membered ring is more stable when the ring is entirely saturated, but that six membered rings are favoured when one or more double bonds are present.

The number of chelating rings :

It has been observed that an increase in the number of rings within a particular chelate structure results in greater stability of the chelates. This is termed chelate effect.

Substitution effect :

The substitution of an atom of a group in the chelating ligand has a pronounced effect on stability. This is because the substituted atom or group affects the nature of the ligand in some ways, (i) It may provide an additional coordinating atom thus increasing the chelating effect with corresponding increase in stability. (ii) An increase in the basicity of the ligand as a result of substitution favours the complex formation, whereas lowering of basicity causes decrease in stability of the complex. (iii) It may interfere with the resonance of the chelating ring. (iv) It may increase the total size of the ligand making it bulky in nature. In the case of bulky ligand, when different groups of neighbouring ligands clash, a distortion of bond angles takes place resulting in the decreased stability.

Nature of coordinating atom :

From the above discussion it can be expected that higher is the basicity of the ligand, greater should be its tendency to form complex.[32] However, it is not so in all the cases, because nature of the coordinating atom also affects the stability of the M-L bond. Due to its more basic character ammonia forms more stable complexes with nontransition metal ions than phosphine and arsine. But in case of transition metal complexes, however, the order of stability is

$$AsH_3 > PH_3 > NH_3$$

As all other factors are common in the above ligands, the nature of the ligand atom has to be held responsible for the difference in the order of the stabilities in case of nontransition and transition metal complexes.

However, there is no uniform pattern of relative coordinating affinities of all ligand atoms for all acceptor molecules or ions, not even when only simple unidentate ligands of closely related analogous structures are considered. The relative affinities are dependent more on the acceptor concerned. It was observed that under comparable conditions, the relative tendency of the alkyls of the V and VI group atoms to combine with trimethyl gallium are $N > P > As > Sb$ and $O > S < Se > Te$, but towards Pt(II), the order appears to be $N < P > As > Sb$ and $O < S > Se < Te$.

However, metals can broadly be classified into two different types. Class A consists of those which form their most stable complexes with the first ligand atom of the each group (N, O and F), whereas class B metal ions are those which form their most stable complexes with the second or subsequent ligand atoms of the groups (P, As, Sb, S, Se, Te and Cl, Br, I).

Nontransition metal ion and the earlier members of the transition series exhibit class A character whereas the later members of the transition series show class B character. The greater stability of M-P, M-As and M-S bonding has been explained in terms of M-L, $d\pi$-$d\pi$ interaction but the extent of M-L π interaction is a question in controversy.

In the ternary systems containing one metal ion and two ligands, formation of complex depends on the property of the metal ion and both the ligands. If the two ligands have significant difference in complexing tendencies, a simple complex is formed between the more complexing ligand and the metal ion while the other ligand remains unbound in solution. However, if complexing tendencies do not differ very much, following types of reactions take place as classified by Martell[33].

(i) Combination of the metal ion with both the ligands simultaneously to form a mixed ligand chelate in a single step or two overlapping steps, reflecting slight difference in the affinities of the ligand for the metal ion

$$A + L + M \rightleftharpoons MLA$$

$$A + L + M \rightleftharpoons ML + A \rightleftharpoons MLA$$

(ii) Formation of a mixed ligand chelate in two distinctly separated steps, reflecting a large difference in the affinities of the ligand for the metal ion.

$$M + A \rightleftharpoons MA \qquad MA + L \rightleftharpoons MAL$$

The resulting mixed ligand chelates should be sterically stable. Otherwise the mixed ligand complex formed disproportionates or there is formation of two single chelates rather than a mixed ligand chelate.

$$2MAL \rightleftharpoons MA_2 + ML_2$$

$$xL + yA + 2M \rightleftharpoons MLx + MAy$$

In the reaction of the first type the solution consists of the species MA, ML_1, MAL, MA_2, ML_2, formation of each being characterised by the formation constants. The mixed ligand formation can be of two types :

$$K^{MA}_{MAL} \quad \text{or} \quad MK^{ML}_{MLA}$$

In the second type of reactions the species present in solution can be MA, MAL and with excess ligand (L) MAL_2. The mixed ligand formation constant is K^{MA}_{MAL} and characterises the reaction

$$MA + L \rightleftharpoons MAL$$

The necessary condition for such systems is that the two ligands must combine with the metal ion in two different pH ranges and the formation of 1:1 MA should be complete in the lower pH range. Species MA should be stable in the higher pH range where the combination of ligand (L) starts.

Various reactions of first and second types have been studied.

Mixed ligand systems containing neutral molecule as primary ligand have been studied potentiometrically by J.I.Watters and R.Dewitt.[34,35] They have studied the systems of the type MAL where M = Cu(II), Ni(II) and A = ethylenediamine, L = oxalate ion. The mixed ligand formation constants K_{MAL} is found to be less than that of K_{ML_1}, the first formation constant of binary system. value. This is explained to be due to the fact that the tendency of L to get bound to aquated metal ion is more than to the metal ion bound with ethylenediamine. Mixed ligand study, where dipyridyl or o-phenanthroline are primary ligands, have also been carried out potentiometrically by Chidambaram and Bhattacharya.[36] The mixed complex Ni(II)DMG dipyridyl was studied by applying high frequency titrimetry technique.[37] Paramagnetic adducts of Ni(II) chelates of monothio β-diketone have been obtained with dipyridyl and o-phenanthroline.[38] Syamal[39] reported the formation of $[\mathrm{Ni\ L'\ L_2}]\mathrm{Cl_2}$ in good yield where L = picolylamine and L' = dipyridyl. The ternary complex phenyl bis(dipy) Ni(II) chelate has also been reported.[40] Systems M.dipy.amino acids have recently been studied by Chidambaram and Bhattacharya.[41]

Formation of diacetato 2,2'-dipyridyl Cu(II) has been reported.[42] The solution studies of mixed ligand complexes of the type Cu.dipy.L where L = polyhydroxy phenol and acids have been detailed by Martell and coworkers.[43] Potentiometric titration techniques have been used in the study of binuclear diolated Cu(II) complexes of the type $[\mathrm{Cu_2(OH)_2L_2}]^{2+}$ where L = dipyridyl or o-phenanthroline or histamine.[44] Narain[45] reported the preparation and characterisation of the mixed ligand complex Cu(II) pthalamide with dipyridyl or o-phenanthroline. Heterochelates of Cu(II) and 2,2'-dipyridyl or o-phenanthroline with biguanide have been prepared and characterised.[46] Dutta and coworkers[47] isolated and characterised several Cu(II) complexes of type Cu(A-A) X_2 , A-A = dipyridyl or o-phenanthroline or 5-nitro-o-phenanthroline and X = NCS, NO_2 or N_3. They also synthesised a number of mixed chelates of Cu(II) containing glycine or α-(DL) alanine and α-α'-dipyridyl, o-phenanthroline or 5-nitro-o-phenanthroline of the type $[Cu(A-A)\ XY]Z.xH_2O$ where Z = Cl, Br, I[48] and also 5-nitro-o-phenanthroline monobiguanide Cu(II) complexes.[49] The temperature jump technique has been used to determine the rate constant for the formation and dissociation of the mixed complex $[Cu.dipy.glycine]^+$ by Sigel and coworkers.[50]

Mixed complexes of type M.dipy.pyridine were studied colorometrically, potentiometrically and ESR spectral studies with number of first row transition metals.[51] Murakami and coworkers have synthesised and characterised Co(III) complexes containing dipyridyl and amino acids.[52] Mixed ligand complexes of type $[Co^{3+}(dipy)Y.]Cl_2\ xH_2O$, Y = bidentate amino acid were studied polarographically.[53] Dutta and coworkers observed that cis-diamine Co(III) sulphate reacts readily with ethylenediamine, o-phenanthroline or dipyridyl liberating ammonia with the formation of the mixed ligand complex.[54] The complexes of Co(II) diphthalamide 2,2'-dipyridyl or o-phenanthroline have been characterised by I.R. spectral studies.[55] Mixed complexes of Co(III) with dipyridyl, o-phenanthroline and paludrine were also studied.[56] Dutta and coworkers[57] have reported the synthesis of heterochelates of Co(III) with dipyridyl, o-phenanthroline and biguanide. Octahedral complexes of Co(II) bis ethylacetoacetate with aromatic heterocyclic amine as dipyridyl or o-phenanthroline have been synthesised.[58] Broomhead and coworkers[59] synthesised and resolved the heterochelates of Co(II) and Cr(II) with the ligand dipyridyl or o-phenanthroline and oxalate ions. Synthesis of octahedral complexes $[Co(A)L_2]\ Cl_2$ where A =

dipyridyl, o-phenanthroline, acetylacetone, L = halides have been described.[60] Preparation and properties of malonato bis dipyridyl Co(III) have been described.[61] Synthesis of glycine oxide Co(III) heterochelates has been reported.[62] Co(III) + dipyridyl + amino acid mixed complexes have been studied polarographically by Maki and Itatani.[63]

Formation of diacetato bis dipyridyl Cr(II) by treatment of Cr(II) acetate with dipyridyl has been described.[64] The new product diacetato dipyridyl bis iso-propylamine Cr(II) has been reported.[65] Crystalline mixed ligand chelates of Cr(III) with dipyridyl or o-phenanthroline halides and acetylacetone have been prepared.[66]

Titanium was spectrophotometrically determined by the formation of mixed ligand compound with dipyridyl and salicylate.[67] Sen and coworkers[68] synthesised the bis dipyridyl dicyano Rh(II) complexes. Chisewell and coworkers[69] attempted the synthesis of halogen coordinated mixed ligand complexes of Ir(III) with 1,10-phenanthroline. $[UCl_3.OEt.(dipy)_2]$ and $[UCl_3.OEt(phen)_2]$ were isolated by Gans and coworkers.[70] The new seleno cyanato complexes of Pd(II) or Pt(II) with dipyridyl have been worked out.[71] The formation of compounds $[MoCl_3$ pyridine o-phenanthroline$]$, $[MoCl_3$ pyridine dipyridyl$]$ has been reported.[72] $[VO(dipy)_3(NCSe)_2]$, $[VO(phen)_3(NCSe)_2]$ have also been prepared.[73] The synergic extraction of Eu(III) bis-o-phenanthroline tris-salicylato complex has been described.[74]

Sigel and coworkers[75-81] have investigated ternary transition metal complexes with dipyridyl as the primary ligand and many monodentate or bidentate secondary ligands coordinated through two oxygen atoms, two nitrogen atoms or one oxygen and one nitrogen atom. Bhattacharya and coworkers[82] have recently reported potentiometrically the system [M.dipy.thio acid] where M = Zn^{2+} or Ni^{2+}.

Mixed ligand complexes containing charged ligand ions as a primary ligand have also been studied by earlier workers.[83-87] X-ray crystallographic analysis of a mixed amino acid complex of L-histidineto L-threoninato Cu(II) hydrate was carried out by Freeman, Huns, Guss, Healy, Martin and Nockolds.[88] Cu(II).histidine and threonine was studied potentiometrically by Martin and others.[89] Mixed coordination of metallic ions with compounds of biological interest for example the system containing Zn^{2+} ion, L-histidine and cyanide ions was studied potentiometrically by Martin and coworkers.[90]

Mixed ligand complex formation studies containing iminodiacetic acid as a primary ligand and hydroxy acids or diamine or amino acids as secondary ligand were carried out by Sharma and Tondon.[91-93] Fridman and coworkers[94] have also carried out the solution study of the mixed ligand complexes of the type NiLX, where L = IMDA or EDTA and X = pyridine, NH_3 or H_2O. Isolation of oxovanadium(IV) heterochelates of type VOL.H_2O.X , L = IMDA, X = pyridine, α-picoline, alanine was reported.[95]

The mixed ligand complexes of Cu(II) and Ni(II) with NTA and glycine were studied spectrophotometrically by Y.J.Israeli.[96] Triple complex Cu.en.NTA wasstudied spectrophotometrically by Kirson and Israeli.[97] Study of Cu.NTA.picoline was carried out by using visible spectral technique.[98] Mixed complex Cu.NTA.oxime was studied polarographically.[99] Mixed complexes of metallic nitrilotriacetate with glutaric acid and aspartic acid were studied by Israeli and Cecchetti.[100] Mixed complex of serine and argenine with M.NTA were also studied.[101] Mixed complex system M.NTA.glycyl.glycine has also been reported.[102] The reaction of metallic NTA with histamine has also been carried out by Israeli and others.[103] The potentiometric study of M.NTA with ammonia has been reported.[104] Tondon and coworkers have studied potentiometrically M.NTA hydroxy acid system.[105] The formation constants of the mixed ligand systems M.NTA.proline were determined by Israeli and coworkers.[106] The formation constants of M.NTA with cycloleucine were calculated at different temperatures by Israeli and others.[107]

Martell and coworkers[33] have determined the stability of the ternary complexes containing U(VI) NTA and hydroxyquinoline sulphonic acid using their own method based on the consideration that U(VI) NTA complex formed at lower pH combines with the secondary ligand at higher pH. The mixed ligand complexes of various transition metal ions containing several secondary ligands have been synthesised.[108-112] Stability constants of mixed ligand systems M.NTA and different amino acids and hydroxy acids and mercapto acids have been reported recently.[113,114] The triple complexes of Niobium and tantalum with catechol and EDTA were studied spectrophotometrically by Babco and Lukachina.[115] Mixed ligand derivatives of Th-EDTA with monohydroxy carboxylic acids was potentiometrically studied by Gupta and Agarwal.[116] Stability constants of mixed ligand complexes of Hg(II) EDTA thiocyanate and bromide were determined spectrophotometrically by Nomura and Toshiaki.[117] Mixed ligand complexes of Th(IV) EDTA with ligands like tiron, catechol, and chromotropic (CTA), gallic and protocatechuic acids were investigated potentiometrically by Sathe, Mahadevan and Shetty.[118] Reaction of imidazole perchlorate $(LH)^+$ with M.EDTA $(My)^{2-}$, resulting in the formation of mixed complex with composition $[MyL]^{2-}$, was studied by Israeli and coworkers.[119] Mixed complexes of Neodymium and Praseodymium EDTA and H_2O_2 were studied by absorption spectral method.[120] Mixed complexes of Zn.EDTA and sulphur containing ligands were studied in solution by Fridman, Dyatlova and Lastovski.[121] Mixed complex of Ce(IV) EDTA and H_2O_2 was studied by absorption spectral analysis.[122] Mixed complexes of rare earths with EDTA and tartaric acid were potentiometrically studied.[123]

The studies in the case of ternary systems MAL, where M = Cu(II) or Ni(II), A = dipy. or o-phen. or hist. or NTA or EDTA and L = catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid, have not been carried out. Such systems have been studied in the present investigation. In order to compare the values, study of the binary systems containing the metal ions and polyphenols has also been carried out. Some compounds have been isolated in solid state and characterised.

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